Changes of UV Optical Properties of Plasma Damaged Low-k Dielectrics for Sidewall Damage Scatterometry

Premysl Marsik[1,2], Adam Urbanowicz[1], Klara Vinokur[3], Yoel Cohen[3], and Mikhail R Baklanov[1]
[1]AMPS, IMEC, Kapeldreef 75, Leuven, 3001, Belgium
[2]UFKL, Masaryk University, Kotlarska 2, Brno, 61137, Czech Republic
[3]NOVA, Weizmann Science Park, Bldg 22, Rehovot, 76100, Israel

ABSTRACT

Porous low-k dielectrics were studied to determine the changes of optical properties after various plasma treatments for development of scatterometry technique for evaluation of the trench/via sidewall plasma damage. The SiCOH porogen based low-k films were prepared by PE-CVD. The deposited and UV-cured low-k films have been damaged by striping O_2Cl_2, O_2, NH_3 and H_2N_2 based plasmas and $CF_4/CH_2F_2/Ar$ etching plasma. Blanket wafers were studied in this work for the simplicity of thin film optical model. The optical properties of the damaged low-k dielectrics are evaluated the using various angle spectroscopic ellipsometry in range from 2 to 9 eV. Multilayer optical model is applied to fit the measured quantities and the validity is supported by other techniques. The atomic concentration profiles of Si, C, O and H were stated by TOF-SIMS and changes in overall chemical composition were derived from FTIR. Toluene and water based ellipsometric porosimetry is involved to examine the porosity, pore interconnectivity and internal hydrophilicity.

INTRODUCTION

Porous low-k dielectric films are introduced as interconnect-dielectric in integrated circuits below 45nm technology node. For the successful implementation of porous films, many technology challenges have to be faced. The desired material must keep low dielectric constant, while being mechanically tough and chemically stable at the same time, must be hydrophobic and resistant against damage during plasma treatments. The effect of various plasma chemistries on low-k dielectrics is intensively studied [1].

To control the level of damage in production conditions, nondestructive and fast optical methods must be used. For correct implementation of optical models for high precision in-situ scatterometry and ellipsometry, optical properties of the low-k materials and their changes during plasma treatments have to be known and understood.

We focused our study to damage that low-k suffers during the photoresist strip and trench/via etching. In most of the cases, the exposition to plasma causes hydrophilisation of the material and subsequent water adsorption from the clean room air humidity. This process is highly undesired, because leads to dramatic increase of k-value, as water has k~80.

The optical properties of SiCOH porogen based low-k dielectrics [2,3] in our range of interest are mostly determined by the properties inherited from silica and by the presence of organic compound of the SiCOH matrix itself as well as the residuals of decomposed porogen. Photoresist striping plasmas act typically on the organic part of the low-k and cause carbon depletion from the low-k volume due to the accessibility through open pores. In some cases, the plasma exposure can cause pore sealing and reduce the volume damage of the dielectric.

EXPERIMENT

We studied two different porogen based low-k dielectrics (denoted as low-k A and low-k B) with target k value 2.5 in the form of non-patterned thin films (with thickness around 200 nm) on silicon substrates. For both dielectrics, the plasma processing recipes are under development and we applied a selection of actual recipes on our samples.

For low-k A, one etching plasma and two different striping plasma chemistries were used. We prepared set of samples based on the low-k dielectric A with varying deposition and curing conditions and damaged the samples by 10 sec flash of NH_3 plasma in ICP (inductively coupled plasma) reactor. Limited number of samples was damaged by O_2 and O_2/Cl_2 based striping plasmas in ICP chamber. To study effect of $CF_4/CH_2F_2/Ar$ ICP etching recipes on the optical properties, the $CF_4:CH_2F_2$ ratio was modified to obtain different etching rates and to control the by-production of polymer residues [4].

In the case of the low-k dielectric B, two different striping recipes were applied on the samples with varying time of treatment to observe the evolution of the changes. First recipe was based on O_2, and performed in CCP (capacitively coupled plasma) reactor during 20 and 30 seconds. Second recipe was based on H_2N_2 chemistry and we treated the samples for 10, 20 and 30 seconds.

The set of samples was completed with referential non-damaged samples of the dielectrics and also initialization layers, based on more dense and non-porous low-k material.

To evaluate the optical characteristics of the samples, we performed spectroscopic ellipsometry measurement in the range from 2 eV to 9 eV, using various angles of incidence between 55 degrees and 85 degrees on nitrogen-purged Sopra GES5 PUV-SE in rotating analyzer configuration.

The measured ellipsometric angles Ψ,Δ were fitted by layered optical models using following algorithm: 1)The optical properties and thickness of initialization layers were obtained independently from single layer samples and were fixed for all next fitting steps. 2) Non-damaged layers were measured and the data were fitted by proper harmonic oscillator model. 3) The thickness of the treated film in total was estimated, using the optical model of undamaged material. 4) The model layer was sliced to two (or three) sub-layers, keeping the total thickness as a starting point and then all the thicknesses and the properties of the top layer (resp. top two) were optimized in iterative steps, while the properties of the bottom layer were kept fixed.

Additional knowledge was gathered from Fourier-transformed infra-red (FTIR) absorption measurements on a Biorad QS2200 ME FTIR system, from water-based and toluene-based ellipsometric porosimetry (EP) using our EP10 tool [5] and from TOF-SIMS (time-of-flight secondary ion mass spectroscopy) atomic concentration (Si, C, O, H) profiles.

RESULTS

Effect of NH_3 strip plasma on low-k A

Set of samples of given low-k dielectric was prepared, varying the deposition and curing conditions and reaching various porosities and compositions [6]. The samples were exposed for 10 seconds to NH_3 plasma in ICP reactor. All the samples were measured by spectroscopic ellipsometry and their properties were evaluated using three layer model, because a model using two layers (top damaged and bottom non-damaged) was not representing well the data. The authors are aware of approximate character of such model. The typical example of the optical properties is plotted in fig. 1a. The absorption band between 3 eV and 7 eV is substantially reduced resulting in porous SiO_2-like top hydrophilic layer. The very top layer exhibit increased refractive index and this effect can be attributed to densification. The FTIR absorbance spectra (not shown) show clear reduction of Si-CH_3 bonds and increase of -OH groups [7].

Water based ellipsometric porosimetry experiment was performed to track changes of the layers upon change of the ambient humidity. In this case, the most damaged sample from the set was chosen for the experiment and two-layer model was used for the evaluation (fig 1b).

Although the set of samples resulted in heterogeneous set of results, a relation between porosity and depth of damage (thickness of two top layers) can be stated. The samples prepared with higher porogen load for target porosity 35% (±3%) exhibit depth of damage 73 ± 5 nm and the samples with target porosity 27% (±2%) exhibit depth of damage 58 ± 6 nm.

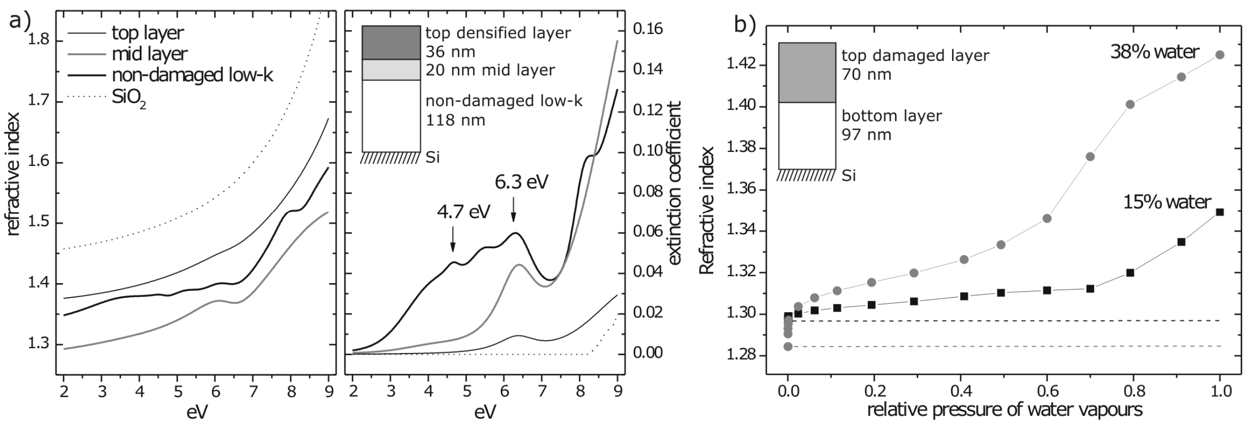

Figure 1 a) Optical properties of NH_3 plasma damaged low-k dielectric (left). The three-layer model reveals reduction of absorption band between 3 eV and 7 eV (attributed to organic compound of the material) in the top layers and densification of the very top layer. Optical properties of SiO_2 are plotted for comparison. b) The optical properties of damaged low-k dielectric change with air humidity (right) as the film becomes hydrophilic. The water based ellipsometric porosimetry (WEP) can detect higher hydrophilicity in the top layer. (Note: the sample and optical model used for WEP experiment differs from the one plotted in graph a)

Effect of O_2/Cl_2 strip plasma on low-k A

The effect of 10 sec exposition of O_2 and O_2/Cl_2 striping plasmas in CCP reactor on dielectric samples is similar to the one of NH_3 plasma. Top carbon depleted layer has been detected by the spectroscopic ellipsometry, but no further densification (fig 2a). The difference between damaged and non-damaged layer can be observed by TOF-SIMS (fig 2b) as decrease in C and H concentration and some increase of Si and O concentration. Ellipsometric porosimetry measurements detect increased pore size and porosity as the organic material is removed from the pore interior.

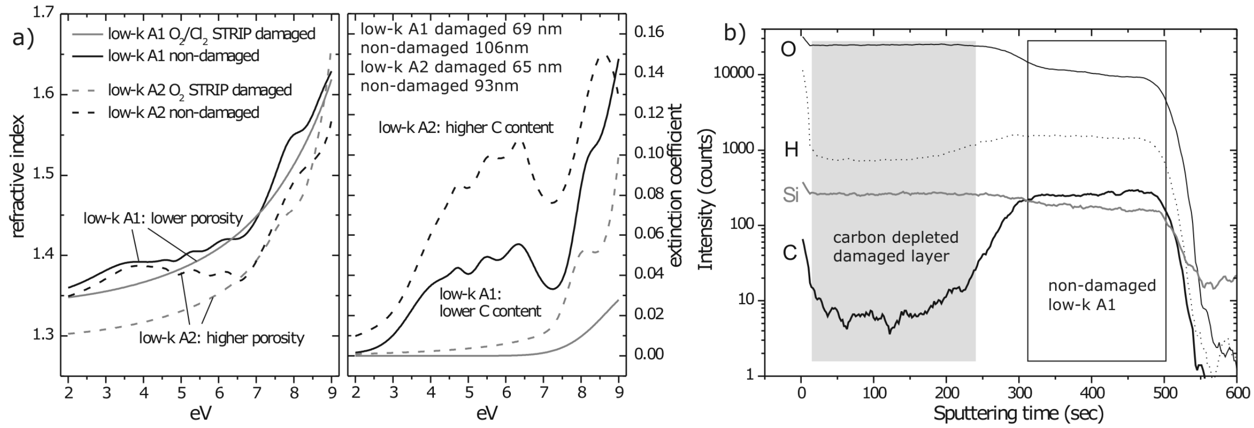

Figure 2 a) Optical properties of two samples of low-k with higher (A1) and lower (A2) porosity damaged by O_2 and O_2/Cl_2 strip plasma (left). Removal of organics from top layer is observed in the ellipsometric spectra as well as in b) the TOF-SIMS profiles of atomic concentrations of Si, C, O and H (right).

Effect of $CF_4/CH_2F_2/Ar$ etch plasma on low-k A

$CF_4/CH_2F_2/Ar$ based CCP chemistries are used for patterning the low-k materials by anisotropic etching. The process is known for leaving fluorocarbon byproducts on the sidewalls and bottoms of the trenches/vias in non-favorable cases. On the blanket wafers, it was observed, that the etching rate can vary, when the CF_4 and CH_2F_2 ratio is changed and also that the process can result as pure deposition of the fluorocarbon for ratio 4:4 [5]. We studied a sample of dielectric A prepared by 16 sec treatment by such plasma and observed 31nm thick layer on the non-damaged material by spectroscopic ellipsometry (fig. 3). This layer is also detected in the TOF-SIMS profile, however, the thickness can not be directly estimated from the profile due to unknown sputtering rates. Fluorocarbon layer of this thickness seals the pores, as can be proven by means of ellipsometric porosimetry.

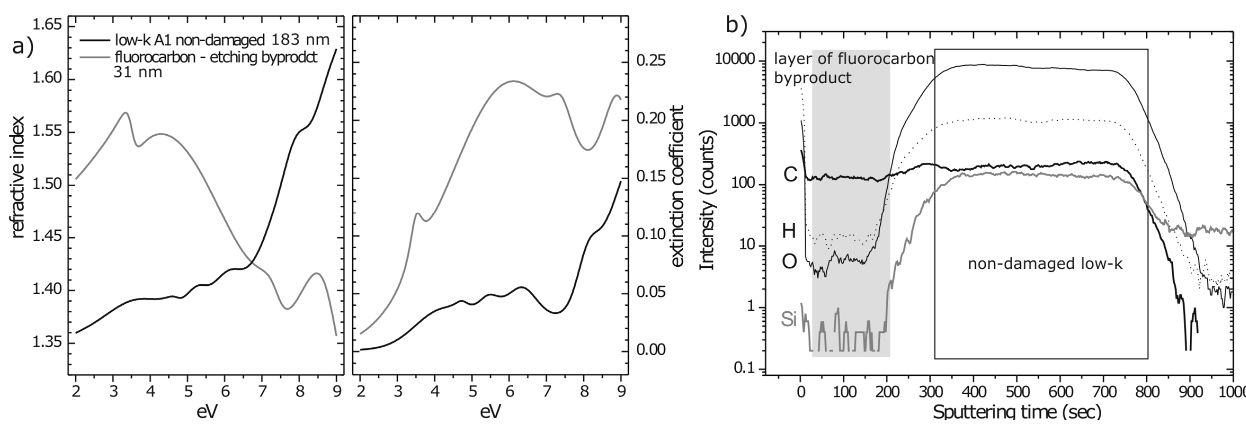

Figure 3 a) Optical properties of fluorocarbon by-product from (4:4:2) $CF_4/CH_2F_2/Ar$ etch plasma. The polymer forms 31nm thick layer on top of the non-damaged film. b) The TOF-SIMS depth profiles shows carbon-rich layer on the sample.

For the standard etching chemistry with ratio (7:1:2 $CF_4/CH_2F_2/Ar$), removal of material is observed without causing significant changes to the optical properties of the low-k. However, the EP experiments sings pore sealing, so some thin layer of fluorocarbon byproduct is expected on the top of the etched blanket low-k. This layer is not clearly visible in the TOF-SIMS profile and direct trial of ellipsometric modeling was not successful, but if the optical properties of the top layer are fixed as obtained from the thicker layer, the model can be improved, resulting in thickness of the fluorocarbon layer equal to 4 nm. It has to be mentioned that the quality of this layer can be different from the deposited fluorocarbon, containing the etching byproducts and diffusing into the near-surface pores.

Effect of O_2 strip plasma on low-k B

We treated the low-k dielectric B by the O_2 plasma in CCP reactor for 20 and 30 seconds. The toluene EP reveals pore sealing and the water EP shows 5% of absorbed water in saturation pressure for both samples (while the non-damaged sample absorbs less than 1%). The determination of top damaged layer from ellipsometric measurements was not clear for this set of samples because of low contrast between refractive index (RI) of damaged and non-damaged sub-layers, but a reduction of UV absorption in the top layer can be reported (fig. 4a).

Effect of H_2N_2 strip plasma on low-k B

Alternative strip plasma for dielectric B based on H_2N_2 CCP chemistry was applied for 10, 20 and 30 seconds on the samples. The EP implicates sealing of pores and low hydrophilisation, resulting in 3% of absorbed water in saturation pressure. The spectroscopic ellipsometry can clearly detect densified top layer with increasing RI with longer treatment time and formation of absorption band around 7.6 eV (fig 4b). The origin of this absorption is not understood and will require further study. The absorption band at 4.1 eV is no longer observed in plasma treated samples.

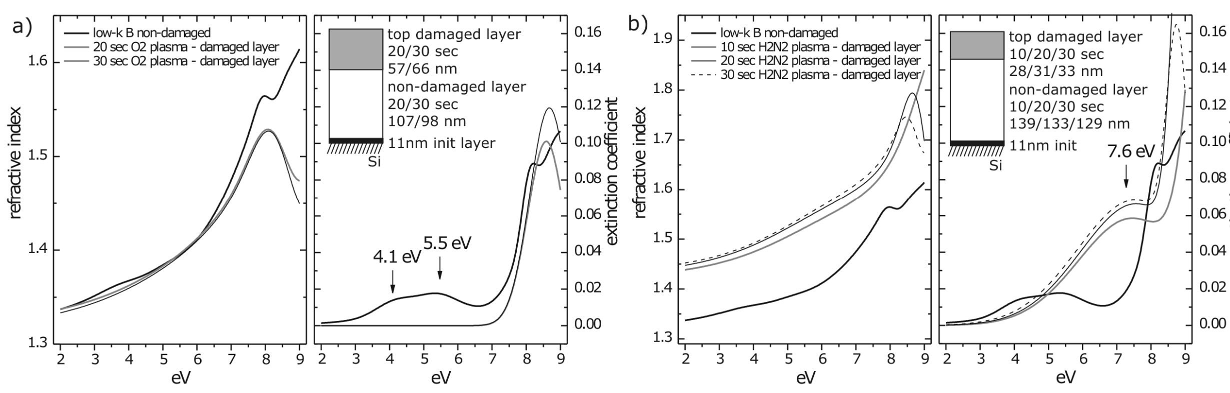

Figure 4 a) Optical properties of non-damaged low-k B and of top layer treated by O_2 plasma in CCP reactor for 20 and 30 seconds. The reduction of absorption bands between 3 and 7 eV is observed, but no significant evolution of RI. b) The optical properties of non-damaged low-k B and of top layer treated by H_2N_2 CCP for 10, 20 and 30 seconds. Increasing RI is detected with increasing treatment time as well as formation of 7.6 eV band.

DISCUSSION

The ellipsometric experiments and modeling efforts are limited by the nature of low-k materials. The inhomogeneities created by non-uniform curing, gradual effect of plasma damage, and also the presence of water in the hydrophilic samples lead to limited accuracy of exact optical constants measured by ellipsometry. All these fact have to be taken into account and studied in more details for exact model construction for scatterometry.

In this stage, first simulations on scatterometry sensitivity were performed using measured properties of low-k A damaged by O_2 plasma in ICP chamber. The feasibility study involved gradient damage on the sidewall and predicted good sensitivity to gradient step parameter, although the gradient profile had to be fixed and linear function was chosen.

Attention has to be given to difference between sidewall damage and modification observed on the blanket wafers. The uniformity of the damaged layer will no longer be present on the sidewall and additional study using electron microscopic techniques has to be performed.

CONCLUSIONS

Collection of low-k films was treated by various plasmas and studied by spectroscopic ellipsometry to evaluate the changes of optical properties of plasma damaged layer. Three main effects of striping plasmas responsible for the changes were found: 1) Removal of carbon content resulting in reduction of UV absorption and lowering the RI. 2) Hydrophilisation of the layer and following shifts in RI related to amount of absorbed water. 3) Densification of the layer resulting in increased RI. Properties of the fluorocarbon byproduct of $CF_4/CH_2F_2/Ar$ etch plasma has been estimated on special sample with fluorocarbon layer deposited by tuning the $CF_4:CH_2F_2$ ratio.

The observed changes of optical properties are, according to first feasibility simulations, sufficient for development of sidewall plasma damage scatterometry.

ACKNOWLEDGMENTS

This work is supported by European Pull Nano project.

REFERENCES

1. D. Shamiryan et al., J. Vac. Sci. Technol. B **20** (5) (2002)
2. P. Marsik et al., Phys. Stat. Sol. (c), accepted (2008)
3. S. Eslava et al., J. Electrochem. Soc., accepted (2008)
4. A. Zaka, unpublished IMEC 2007
5. M. R. Baklanov, K. P. Mogilnikov, Microelectron. Eng., **64**, 335 (2002)
6. P. Marsik, in preparation 2008
7. A. Grill, D. A. Neumayer, J. Appl. Phys., **94**, 10, 6697 (2003)